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Precipitation Under Cyclic Strain in Solution-Treated Al-4wt%Cu II: Precipitation Behavior

Adam Farrow[1] and Campbell Laird[2]

[1]Los Alamos National Laboratory; MS E574 Los Alamos, NM 87544, afarrow@lanl.gov
[2]University of Pennsylvania; 3231 Walnut St. Philadelphia, PA 19104

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Abstract

Solution-treated Al-4wt%Cu was strain-cycled at ambient temperature and above, and the precipitation behavior investigated by Transmission Electron Microscopy (TEM). In the temperature range 100°C to 200°C, precipitation of Θ" appears to have been suppressed, and precipitation of theta-prime promoted. Anomalously rapid growth of precipitates appears to have been facilitated by a vacancy super-saturation generated by cyclic strain, with a diminishing effect observed at higher temperatures due to the recovery of non-equilibrium vacancy concentrations. The Θ' precipitates generated under cyclic strain are considerably smaller and more finely dispersed than those typically produced via quench-aging due to their heterogeneous nucleation on dislocations, and possess a low aspect ratio and rounded edges of the broad faces, due to the introduction of ledges into the growing precipitates by dislocation cutting. Frequency effects indicate that dislocation motion, rather than extremely small precipitate size, is responsible for the reduction in aspect ratio.

Introduction

Accelerated hardening kinetics under cyclic strain reported in a companion paper are explored via a line of transmission electron microscope studies to determine the nucleation and growth behaviors of precipitates formed under cyclic strain. Measurements taken from TEM images are used to estimate precipitate growth rates, enhanced diffusivities under cyclic strain, elevated vacancy concentrations, and characterize unusual precipitate aspect ratios.

Experimental Details

Following processing described in a companion paper, dog-bone specimens of Al-4wt%Cu machined parallel to the rolling direction of their parent plate were annealed in molten salt at 540°C for 10 minutes, and were quenched into ice water. Immediately following quenching, they were strain-cycled at ε_p=+/- 0.001, 1 Hz, ε_p=+/- 0.0025, 0.4 Hz, and at ε_p=+/- 0.005, 0.2 Hz, at temperatures of 25°C, 100°C, 175°C and 200°C. Tests performed at ε_p=+/- 0.001, 1 Hz, and ε_p=+/- 0.0025, 0.4 Hz were interrupted at equal accumulated strain to the strain accumulated at failure in tests run at ε_p=+/- 0.005, 0.2 Hz at each temperature. Thus, each specimen accumulated equal plastic strain and spent equal time at temperature due to the inverse variation of test frequency with strain amplitude. An additional test was run at 200°C, ε_p=+/- 0.005, 0.027 Hz (100 cycles/Hr) to assess the effects of frequency. Following testing, samples were rapidly cooled by raising the pressure of air fed to the furnace and turning off the heating elements.

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TEM foils of each specimen were then prepared by cutting transverse to the stress axis with a jeweler's saw to 0.5mm sections, chemical thinning in 25g NaOH in 100 mL H_2O at 25°C, and electropolishing by the window method in 25mL fuming nitric acid in 75 mL methanol at 8V, -30°C. 3mm disks were then punched from the thinned foils and mounted in a double-tilt holder in a JEOL JEM 2010 transmission electron microscope. Bright-field imaging and selected area diffraction were used to characterize precipitates formed during mechanical testing. Following imaging, a representative sampling of at least 25 precipitates from each specimen displaying precipitation were measured in both length and thickness, and these results were tested against the Zener-Hillert equation for plate lengthening to estimate the diffusivity during testing of each specimen.

Results and Discussion

At 25°C no precipitation was observed, likely due to the short test duration (800 seconds) failing to provide sufficient time for nucleation of precipitates, even given the presence of plentiful dislocations to act as nucleation sites. The dislocation structure formed during these tests appeared largely similar to that observed in pure aluminum [1], consisting of loose tangles of dislocations with small prismatic loops.

At 100°C, fine nucleation of Θ' precipitates was observed in strained specimens, primarily nucleated on dislocations. An example of the structure thus generated can be seen in Figure 1. Precipitates can be seen preferentially nucleating on dislocations, and are confirmed via Selected Area Diffraction (SAD) as Θ', despite their small size, and the relatively short testing time (32 minutes) at 100°C, where Θ" precipitates might be expected. The apparent absence of Θ" implies that not only is Θ' preferentially nucleating, but that cyclic strain inhibits the growth of Θ", as only an extremely small volume fraction of Θ' was observed, suggesting that competitive growth alone cannot account for the absence of Θ".

At 175°C, control specimens annealed on the testframe in the absence of cyclic strain show Θ" precipitates, as expected, but in all cyclic strain tests performed, Θ' precipitates are formed to the apparent exclusion of Θ". Very little residual dislocation density is apparent, as recovery during cyclic straining has largely annealed out dislocations.

At 200°C, Θ" precipitates are formed in unstrained specimens, as shown in Figure 2. In strained specimens, Θ' rapidly forms, and appears to be sheared by dislocation shuttling under cyclic strain, following a mechanism originally proposed by Bhat [2]. This mechanism was originally proposed to explain precipitate dissolution in larger Θ' precipitates, and the nucleation of Θ on Θ' precipitates under cyclic strain. Slower growth of precipitates was observed in the test cycled at 0.027 Hz, suggesting that the rate of accumulation of plastic strain as well as the plastic strain amplitude helps to control the diffusivity under cyclic strain.

On the basis of the measured average lengths and thicknesses of precipitates for each test, diffusivities were calculated from the Zener-Hillert equation for plate lengthening (Eq. 1).

$$G = \frac{D(\chi\alpha - \chi\alpha\gamma)}{4r(\chi p - \chi\alpha\gamma)} \qquad (1)$$

Where G = the precipitate lengthening rate, D = the diffusion coefficient, r = half the precipitate thickness, and $\chi\alpha$, χp, and $\chi\alpha\gamma$ are the solute concentrations in the matrix, precipitate, and at the matrix/precipitate interface, respectively. Given the diffusivities thus calculated and taking the free energy of formation for a vacancy in Al as 0.63 eV [3], the free energy of vacancy motion can be calculated from previous authors' [4-8] data as 0.45 eV, via Eq. 2.

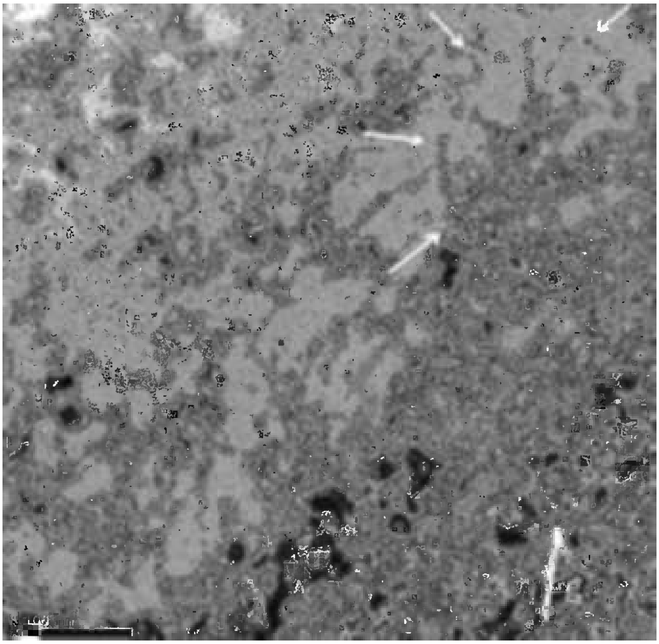

Figure 1. Structure generated at 100°C εp = +/- 0.005, 0.2Hz, 385 cycles (32 minutes) showing precipitation on bowed dislocation (arrowed). g=111, zone axis=[112].

$$D = \frac{1}{6} z \alpha^2 \nu e^{-\left(\frac{\Delta E_v}{kT}\right)} e^{-\left(\frac{\Delta E_m}{kT}\right)} \qquad (2)$$

Where D = diffusivity, z = coordination number, α = inter-atomic distance, ν = vibrational frequency of the lattice (taken here as 10^{13}). If the diffusivities calculated in this study are used with the free energy of

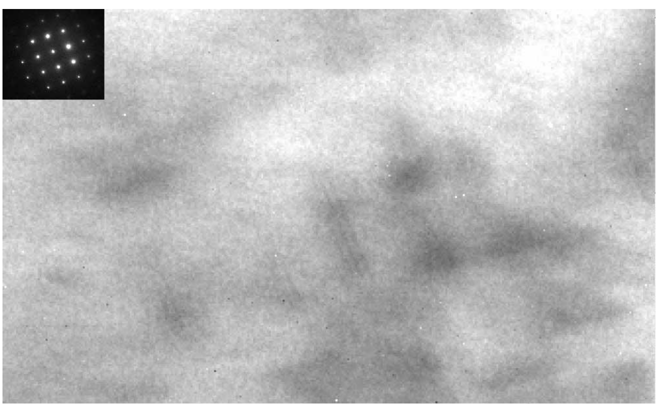

Figure 2. Θ'' precipitates formed in an unstrained control specimen annealed at 200°C for 800 seconds. Field of view = 97nm.

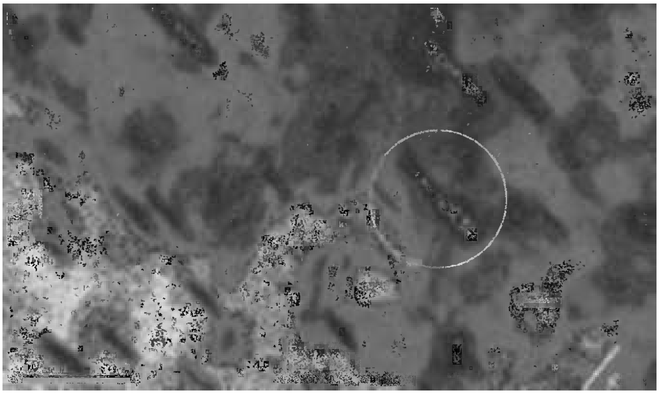

Figure 3. Transmission electron micrograph, showing twisting of Θ' precipitate following repeated shearing. g=(111) of a [110] zone axis. Specimen machined in the rolling direction, tested at εp = +/- 0.0025 to failure at 280 cycles, 0.4 Hz (700 seconds).

motion of 0.45eV, vacancy concentrations can then be approximated for each specimen. The results of this calculation are shown in Figure 5.

Of note is that above recovery temperatures, the vacancy super-saturation begins to drop, as greater mobility allows vacancies to find sinks faster. Thus for a given strain amplitude, a higher vacancy concentration will be present at lower temperatures, since vacancy generation by jog dragging or partial dislocation annihilation will allow for athermal generation of a vacancy super-saturation, while the ability of the vacancies to find sinks is reduced. One obvious anomaly generated by this experimental approach can be seen in the unstrained specimen annealed at 100°C. Due to the annealing above the solvus and quench immediately preceding this intermediate anneal, it seems likely that this super-saturation is residual from the quench. The concentration of thermal vacancies during the initial anneal above the solvus is calculated as $1.25*10^{-4}$, and given the rapid quench and immediate intermediate anneal, it is not unreasonable to believe that this residual vacancy concentration may have accelerated the diffusion kinetics in the specimen sufficiently to accelerate precipitate growth rates to a level corresponding to the steady-state concentration of $6*10^{-7}$ calculated.

A further observation pertains to the aspect ratios of precipitates measured in this study, shown in Figure 6. Given precipitate twisting as evidence of precipitate shearing as proposed by Bhat [2], ledges should be created at precipitate surfaces , allowing for more rapid thickening of precipitates during cyclic strain. Aaronson et. al. [9] calculated energies for Θ':α interfaces as 40 ergs/cm^2 along the broad faces of plate-like precipitates, and as 445 ergs/cm^2 along the edges. Thus the equilibrium aspect ratio of precipitates should be expected to be somewhere around 11. Previous authors, (e.g. [10]) have typically measured aspect ratios on the order of 40 for Θ', suggesting that ledge nucleation limits the thickening of plates, as they tend to form at greater than equilibrium aspect ratios. In this study, the continual cutting of growing precipitates leads to an apparent reduction is aspect ratios, and an expected temperature and frequency sensitivity. Since the diffusion rate increases with increasing temperature, and the strain frequencies sampled remain the same across all temperatures, we should expect to see larger aspect ratios at higher temperatures, which appears to be case. Precipitates formed at 100°C show a markedly lower aspect ratio than those formed at higher temperatures. In addition, the specimen strained at ε_p=+/- 0.005, 100 cycles/hr (0.027Hz) shows a much greater aspect ratio than those formed at

ε_p=+/- 0.005, 0.2 Hz. Sankaran [11] found a transient increase in Θ' thickening rates following monotonic deformation, but attributed it to a transient increase in diffusivity due to the accelerated diffusion kinetics caused by deformation.

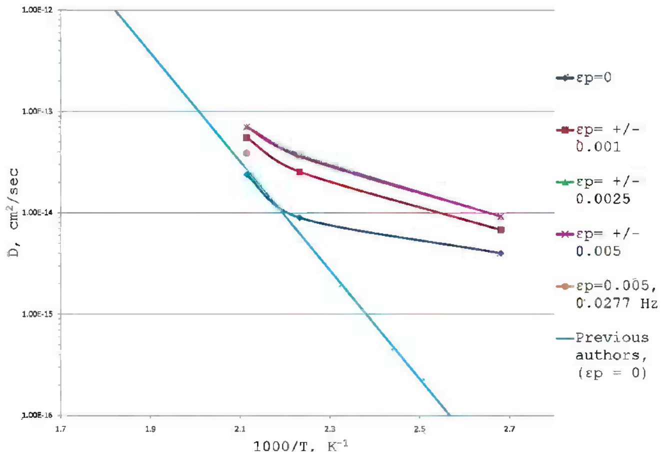

Figure 4. Diffusivities measured in this study as a function of inverse temperature and plastic strain amplitude. Diffusivities for ε_p=+/- 0.0025, 0.4 Hz and ε_p=+/- 0.005, 0.2 Hz overlay. The solid line shows an average of previous authors' interdiffusivities generated by Sankaran [10].

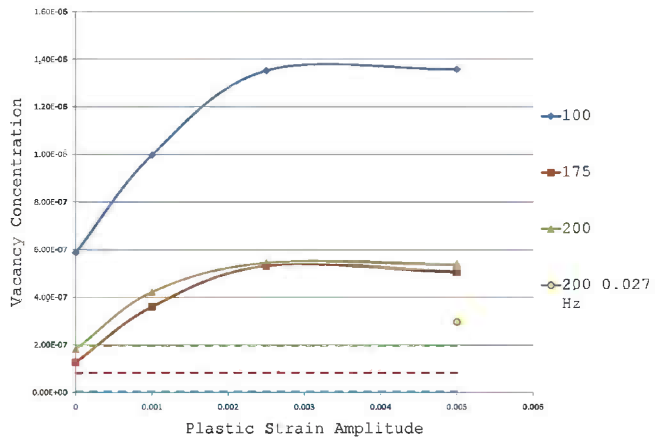

Figure 5. Vacancy concentrations calculated for this study. The dotted lines show the calculated equilibrium thermal vacancy concentrations.

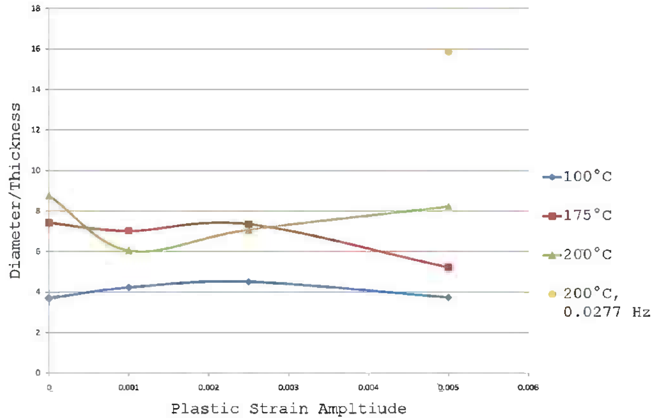

Figure 6. Average aspect ratios of precipitates measured in this study.

Conclusions

1. Cyclic strain effectively suppresses the formation of Θ" and promotes formation of Θ'
2. Diffusion kinetics are appreciably accelerated during cyclic strain at low temperatures, but increased vacancy mobility limits the observed super-saturation at recovery temperatures.
3. The suppression of Θ" precipitates allows for the creation of smaller Θ' precipitates than are observed in conventional quench-aging, as Θ' tends nucleate on dislocations under cyclic strain, rather than on Θ" precipitates, as observed in quench-aging. This allows for smaller nuclei, and nucleation outside of already Cu-enriched precipitates.
4. The aspect ratios of precipitates formed under cyclic strain are significantly reduced via increased thickening rates as ledges are nucleated athermally via dislocation cutting.

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